SUPPORTING INFORMATION

Efficient and Selective \textit{N}-Methylation of Nitroarenes under Mild Reaction Conditions

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1. Catalyst characterization.

**Figure SI1.** $^1$H NMR spectrum of the complex [Mo$_3$Pt(PPh$_3$)$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_3$ in CD$_2$Cl$_2$.

**Figure SI2.** $^{13}$C NMR spectrum of the complex [Mo$_3$Pt(PPh$_3$)$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_3$ in CD$_2$Cl$_2$.

**Figure SI3.** ESI mass spectrum of the complex [Mo$_3$Pt(PPh$_3$)$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_3$ in CH$_3$CN at 20 V.

**Figure SI4.** Cyclic Voltammogram recorded on a CH$_2$Cl$_2$ solution containing 3$^+$ (a) and 1$^+$ (b) at scan rate of 100mV/s (vs Ag/AgCl).

2. Conditions optimization for the $N$-methylation of $p$-nitrotoluene (1a).

**Table SI1.** Screening of silanes.

**Table SI2.** Influence of the solvent on the catalytic $N$-methylation of 1a.

3. ESI mass spectra from the reaction mixture during the $N$-methylation of 1a.

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**Figure SI6.** ESI mass spectrum from the mixture of [Mo$_3$S$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_3$ (1(BF$_4$)) (0.003 mmol) and Pt(PPh$_3$)$_4$ (2) (0.001 mmol) in THF after 10 minutes stirring at room temperature.

4. Reaction pathway investigation.

**Scheme SI1.** Proposed pathways for the direct $N$-methylation of nitroarenes with formic acid.

5. Characterization data of isolated products.

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7. $^1$H NMR and $^{13}$C NMR spectra of isolated products.
1. Catalyst characterization

Figure S11. $^1$H NMR spectrum of the [Mo$_3$Pt(PPh$_3$)$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_3$ complex in CD$_2$Cl$_2$.

Figure S12. $^{13}$C NMR spectrum of the [Mo$_3$Pt(PPh$_3$)$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_3$ complex in CD$_2$Cl$_2$. 

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**Figure SI3.** ESI mass spectrum of the $[\text{Mo}_3\text{Pt(PPh}_3)_3\text{Cl}_3\text{(dmen)}_3](\text{BF}_4)$ complex ($3(\text{BF}_4)$) in CH$_3$CN at 20 V.

**Figure SI4.** Cyclic Voltammogram recorded on a CH$_2$Cl$_2$ solution containing $3^+$ (a) and $1^+$ (b) at scan rate of 100 mV/s (vs Ag/AgCl).
2. Conditions optimization for the $N$-methylation of $p$-nitrotoluene (1a).

Table SI1. Screening of silanes.[a]

<table>
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<tr>
<th>Entry</th>
<th>Silane</th>
<th>Conversion [%][b]</th>
<th>Yield 2a [%][b]</th>
<th>Yield 3a [%][b]</th>
<th>Yield 4a [%][b]</th>
<th>Yield 5a [%][b]</th>
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<td>0</td>
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[a] Reaction conditions: 1a (0.1 mmol), HCO$_2$H (8.5 equiv.), Silane (10 equiv.), Catalyst (3 mol%), THF (2 mL), 18 h, 70$^\circ$C. [b] Determined by GC analysis using $n$-hexadecane as an internal standard.
Table SI2. Influence of the solvent on the catalytic N-methylation of 1a.[a]

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion [%][b]</th>
<th>Yield 2a [%][b]</th>
<th>Yield 3a [%][b]</th>
<th>Yield 4a [%][b]</th>
<th>Yield 5a [%][b]</th>
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<td>0</td>
<td>2</td>
<td>97</td>
</tr>
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</table>

[a] Reaction conditions: 1a (0.1 mmol), HCO₂H (8.5 equiv.), PhSiH₃ (10 equiv.), Catalyst (3 mol%), Solvent (2 mL), 18 h, 70°C. [b] Determined by GC analysis using hexadecane as an internal standard. [c] The urea intermediate 1,3-dimethyl-1,3-di-p-tolylurea is detected by GC-Mass.

3. ESI mass spectra from the reaction mixture during the N-methylation of 1a.

![ESI mass spectrum](image)

Figure SI5. ESI mass spectrum from the N-methylation reaction after 8 hours.
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Figure SI6. ESI mass spectrum from the mixture of [Mo$_3$S$_4$Cl$_3$(dmen)$_3$](BF$_4$)$_2$ (1(BF$_4$)) (0.003 mmol) and Pt(PPh$_3$)$_4$ (2) (0.001 mmol) in THF after 10 minutes stirring at room temperature.

4. Reaction pathway investigation.

Scheme SI1. Proposed pathways for the direct $N$-methylation of nitroarenes with formic acid in the presence of the heterobimetallic 3$^+$ catalyst.
5. Characterization data of isolated products.

N,N,4-trimethylaniline: $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.03 (d, $J = 8.6$ Hz, 2H), 6.66 (d, $J = 8.6$ Hz, 2H), 2.88 (s, 6H), 2.23 (s, 3H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 149.53, 130.00, 126.39, 113.56, 41.43, 20.48; MS (EI): $m/z$ (rel. Int) 135.

3-Chloro-N,N-dimethylaniline: $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.13 (t, $J = 8.1$ Hz, 1H), 6.70 – 6.56 (m, 3H), 2.94 (s, 6H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 152.26, 135.31, 130.50, 116.33, 112.51, 111.04, 40.69; MS (EI): $m/z$ (rel. Int) 155.

3-iodo-N,N-dimethylaniline: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.06 – 7.02 (m, 2H), 6.96 – 6.91 (m, 1H), 6.69 – 6.65 (m, 1H), 2.93 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 151.68, 130.51, 125.33, 121.21, 111.70, 95.67, 40.45; MS (EI): $m/z$ (rel. Int) 247.
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\[
\text{N,N-dimethyl-4-(methylthio)aniline: } ^1H \text{ NMR (300 MHz, CD}_2\text{Cl}_2 \delta 7.14 (d, } J = 9.0 \text{ Hz, 2H), } 6.58 (d, } J = 8.9 \text{ Hz, 2H), 2.81 (s, 6H), 2.29 (s, 3H); } ^{13}C \text{ NMR (75 MHz, CD}_2\text{Cl}_2 \delta 134.63, 131.47, 128.45, 113.83, 41.02, 19.24; MS (EI): } m/\zeta \text{ (rel. Int) 167.}
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\[
\text{N,N-dimethyl-3-vinylaniline: } ^1H \text{ NMR (300 MHz, CD}_2\text{Cl}_2 \delta 7.23 (t, } J = 7.6 \text{ Hz, 1H), } 6.88 - 6.77 (m, 2H), 6.77 - 6.65 (m, 2H), 5.78 (d, } J = 17.6 \text{ Hz, 1H), 5.25 (d, } J = 10.8 \text{ Hz, 1H), 3.00 (s, 6H); } ^{13}C \text{ NMR (75 MHz, CD}_2\text{Cl}_2 \delta 151.61, 138.84, 138.39, 129.65, 115.06, 113.46, 112.88, 111.08, 40.94; MS (EI): } m/\zeta \text{ (rel. Int) 147.}
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\[
\text{Methyl 4-(dimethylamino)benzoate: } ^1H \text{ NMR (400 MHz, CD}_2\text{Cl}_2 \delta 7.76 (d, } J = 9.1 \text{ Hz, 2H), } 6.56 (d, } J = 9.1 \text{ Hz, 2H), 3.72 (s, 3H), 2.92 (s, 6H); } ^{13}C \text{ NMR (101 MHz, CD}_2\text{Cl}_2 \delta 167.72, 153.99, 131.58, 117.44, 111.22, 51.79, 40.39; MS (EI): } m/\zeta \text{ (rel. Int) 179.}
\]
6-(dimethylamino)-2H-chromen-2-one: $^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ 7.65 (d, $J = 9.5$ Hz, 1H), 7.20 (d, $J = 9.1$ Hz, 1H), 6.97 (dd, $J = 9.1$, 3.0 Hz, 1H), 6.70 (d, $J = 3.0$ Hz, 1H), 6.32 (d, $J = 9.5$ Hz, 1H), 2.96 (s, 6H); $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 161.52, 148.05, 146.58, 144.03, 119.58, 117.42, 117.22, 116.97, 109.50, 41.01; MS (EI): $m/\chi$ (rel. Int) 189.

$N,N$-dimethyl-4-(pyridin-4-ylmethyl)aniline: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.41 – 8.36 (m, 2H), 7.08 – 7.02 (m, 4H), 6.73 – 6.66 (m, 2H), 3.85 (s, 2H), 2.92 (s, 6H); $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ 151.97, 149.95, 130.13, 128.27, 127.42, 124.59, 113.39, 41.02, 40.77; MS (EI): $m/\chi$ (rel. Int) 212.

6. References.

7. $^1$H NMR and $^{13}$C NMR spectra of isolated products.
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